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XAD-2 Thermal Blank Determination

Duke Univ.
Durham, NC

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

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Sampling	Stationary Sources	14B 07C
Analyzing	Environmental Assessment	
Assessments		
Polymers	XAD-2 Resin	07D
Adsorbents	Thermal Blanks	11G
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by

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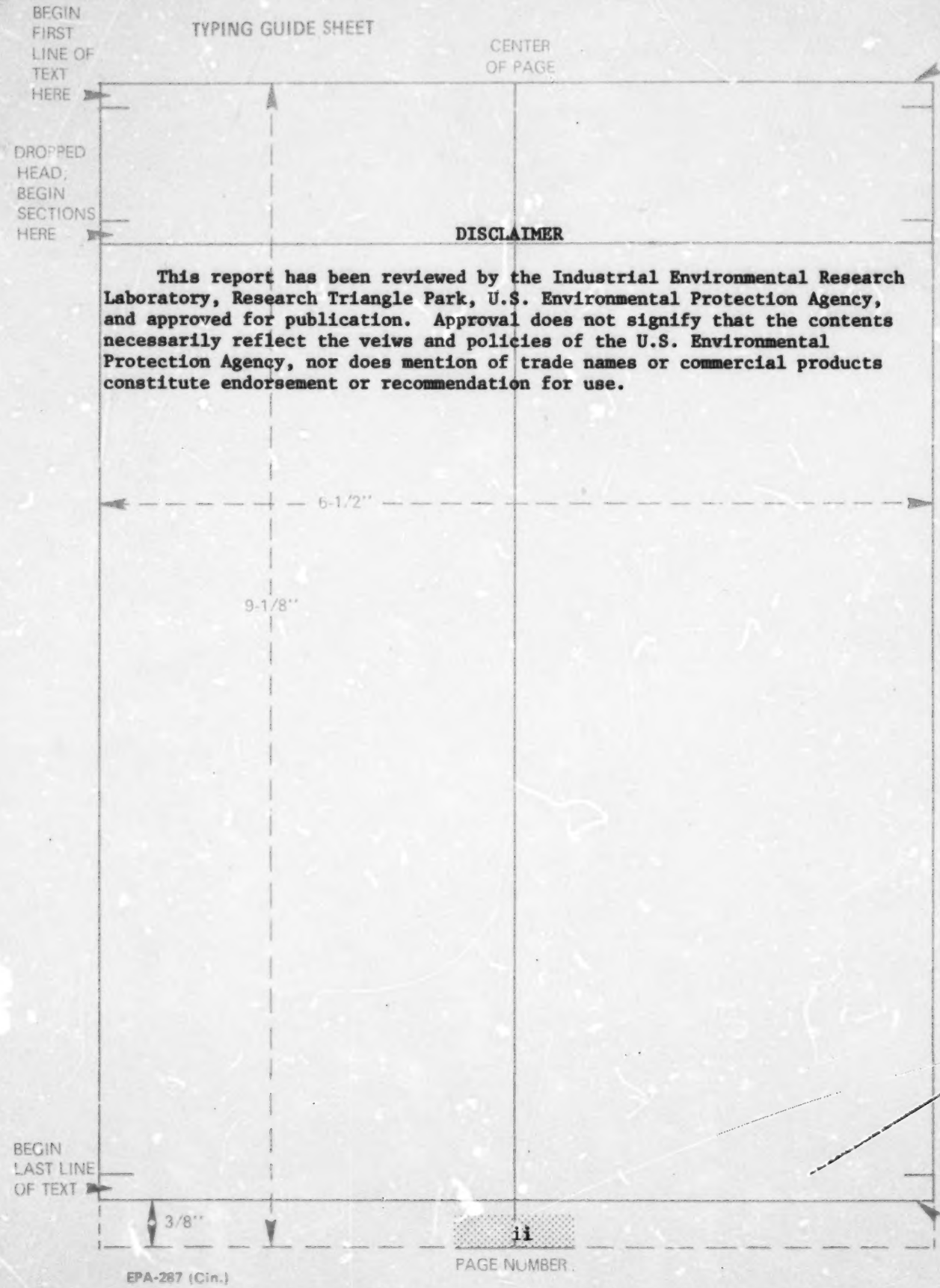
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ABSTRACT

The primary objective of this study was to achieve a qualitative and quantitative determination of the thermal blank produced by XAD-2 resin as used in the Level 1 Environmental Assessment Procedure. Accurate determination of the nature of species collected from the environment requires that the trapping material used produce only a relatively small, well-defined blank when carried through the collection procedure. Simulated-use conditions were utilized to evaluate this blank in these studies. In addition to the thermal study, a brief examination of the blank due to materials present in the resin before cleaning and due to materials produced by physical agitation of the resin was also carried out.

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This report was submitted in fulfillment of Contract No. R-805494-01 by Duke University under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period 1 May 1978 to 1 June 1979, and work was completed as of 1 June 1979.

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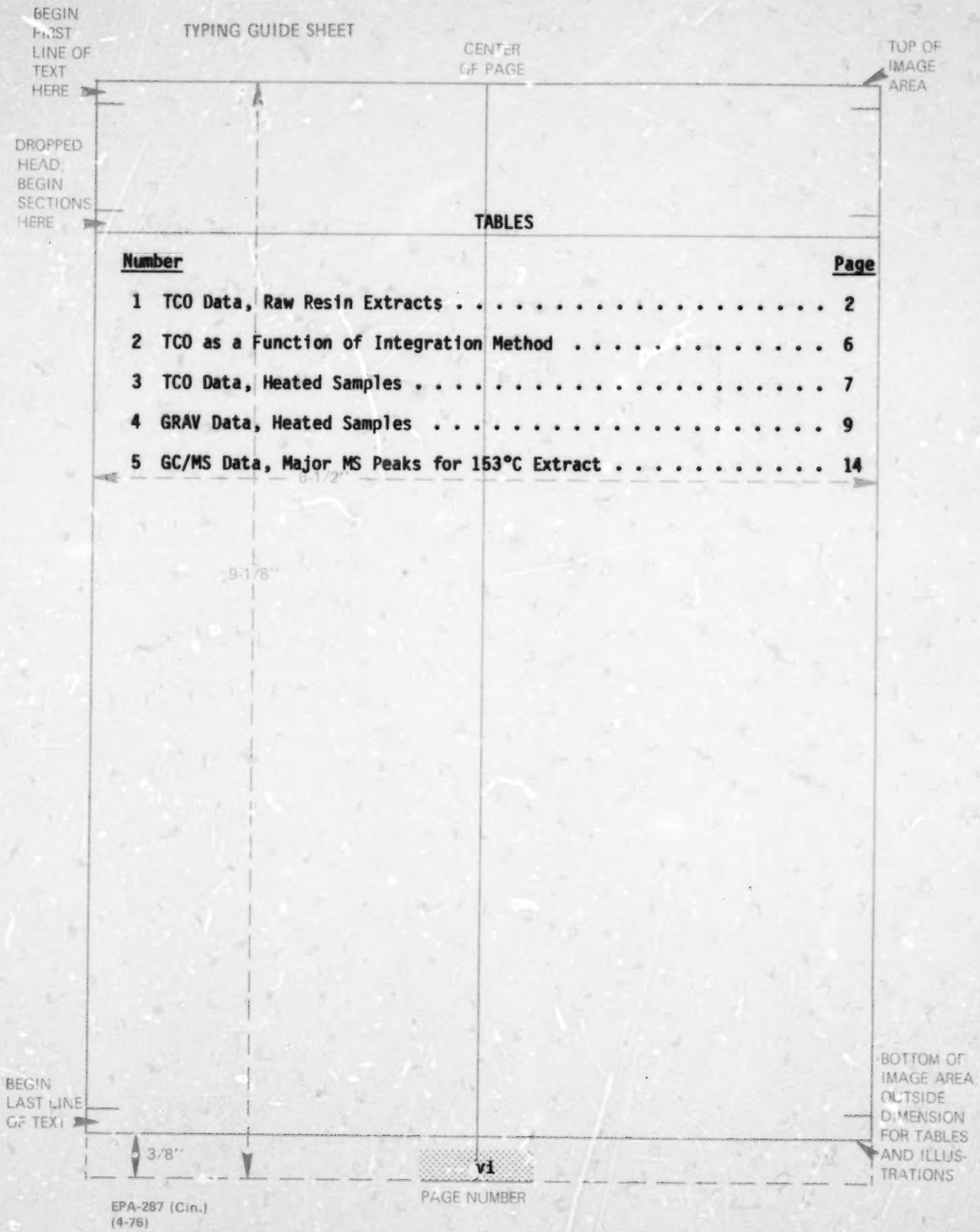
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Section 1

INTRODUCTION

Porous polymer adsorbents have proven to be effective for collection and preconcentration of organic materials in air streams. As part of the Environmental Protection Agency, Industrial Environmental Research Laboratory-RTP Level 1 Procedure (1) for environmental assessement, XAD-2 resin, a polystyrene-divinylbenzene porous polymer, is used in an adsorbent trap for the collection of volatile organic species. This resin trap is part of the Source Assessment Sampling System (SASS) which was designed specifically for environmental sampling of gaseous streams. One of the prerequisities for the selection of a material used for trapping species from such a stream is that the material introduce as small a blank value as possible in relation to the sample collected. If this blank is of sufficient size, both qualitative and quantitative determination of the materials trapped by the resin becomes difficult. The purpose of this study was to examine the stability of XAD-2 resin, particularly its thermal stability under simulated use conditions. While the bulk thermal stability of the resin may be good, introduction of contaminants on the milligram scale can be sufficient to give a large blank value in relation to the total collected material. In the present study, the magnitude of the thermally-induced blank was assessed primarily by measurement of the Total Chromatographable Organic (TCO) fraction of the resin extract using procedures detailed in (1). In addition, a gas chromatography/mass spectroscopy (GC/MS) study of several of the extracts was carried out to identify the components of the blank.

Some previous work in this area was carried out by Arthur D. Little, Inc. (Personal communication, Larry Johnson, EPA-RTP), although the resin samples were subjected to lower temperatures than those in this study, and the quantitative procedures used were to some degree different. Nevertheless, some of those results are relevant to this new study, and reference will be made where appropriate. Earlier studies by other investigators of the thermal degradation of polystyrene and its degradation products were found to be useful in interpretation of the GC/MS results, even though the experimental conditions were vastly different (2). In addition to the thermal blank studies, the nature of the material extracted upon cleaning of the resin was studied, and a brief examination of the abrasive stability of the resin was made to determine whether physical handling could contribute to an increase in the overall blank.

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Section 2

RESULTS AND DISCUSSION

Studies of the methylene chloride extract of the unheated resin indicated the need for extensive cleaning in order to remove all extractable materials from the resin. For the 40 ml samples used in this study, on the order of four to six 24 hour extractions, using fresh methylene chloride every 24 hours, were necessary before a TCO determination on the concentrated extract yielded an undetectable amount of material. Chromatograms of a typical initial and final extract along with a methylene chloride blank injection are shown in Figures 1-3. All these data were obtained with a flame ionization sensitivity of 1×10^{-11} amperes full scale. Data in

TABLE 1. TCO DATA, RAW RESIN EXTRACTS

Sample	mg of TCO/40 ml resin
First 48 hour unconcentrated extract	184
First 48 hour concentrated (10 ml) extract	31
Second 48 hour unconcentrated extract	99
Second 48 hour concentrated (10 ml) extract	4.4
First 48 hour unconcentrated extract	Lost Sample
First 48 hour concentrated (10 ml) extract	23
Second 48 hour unconcentrated extract	110
Second 48 hour concentrated (10 ml) extract	1
First 24 hour unconcentrated extract	140
First 24 concentrated (10 ml) extract	31

Table 1 relates the amounts of TCO material actually measured for two samples cleaned by this procedure. Note that these weights are for only 40

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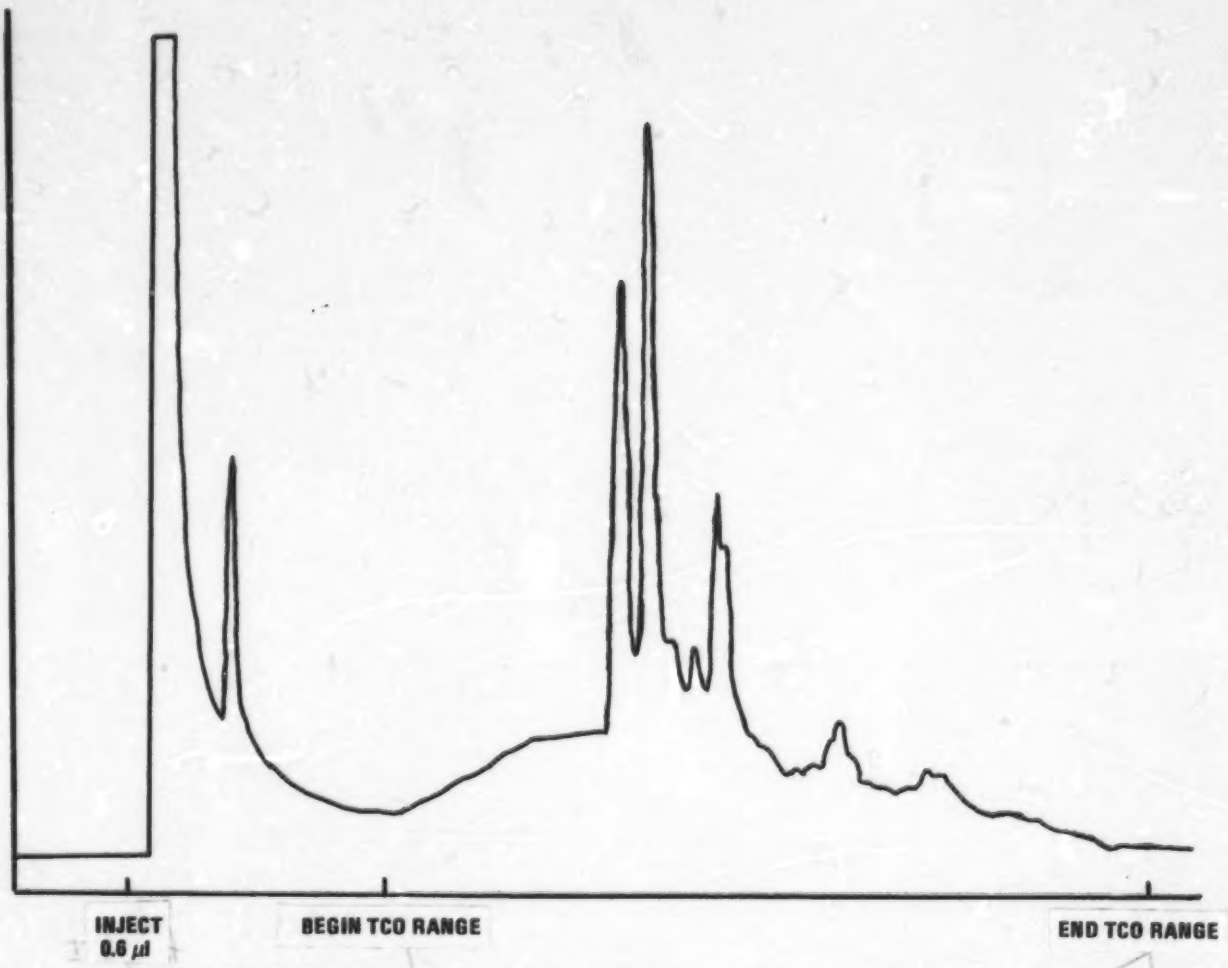

Figure 1. First 48 hour methylene chloride extract of uncleaned resin.

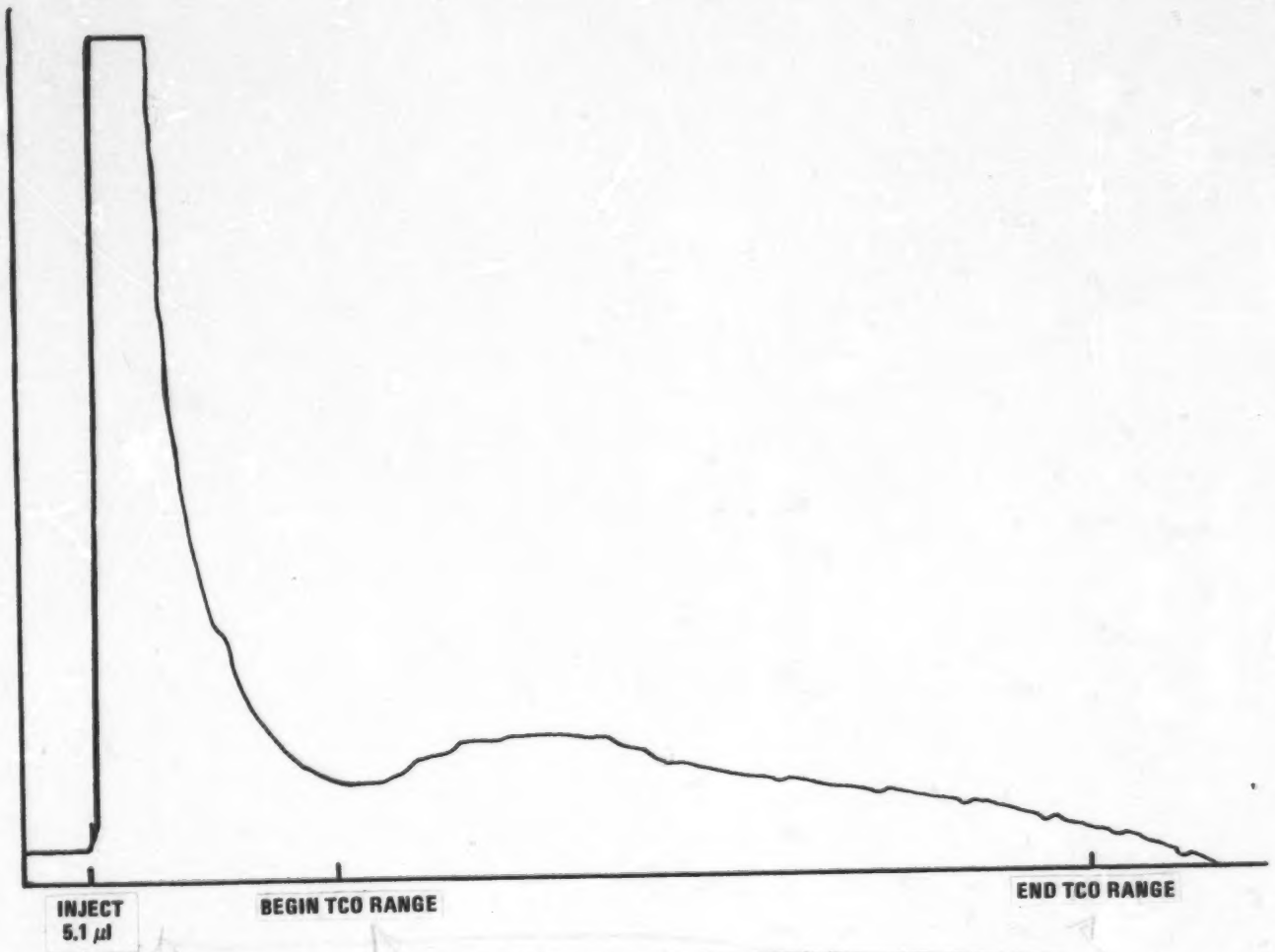

Figure 2. Second 48 hour methylene chloride extract of uncleaned resin, 10 ml concentrate.

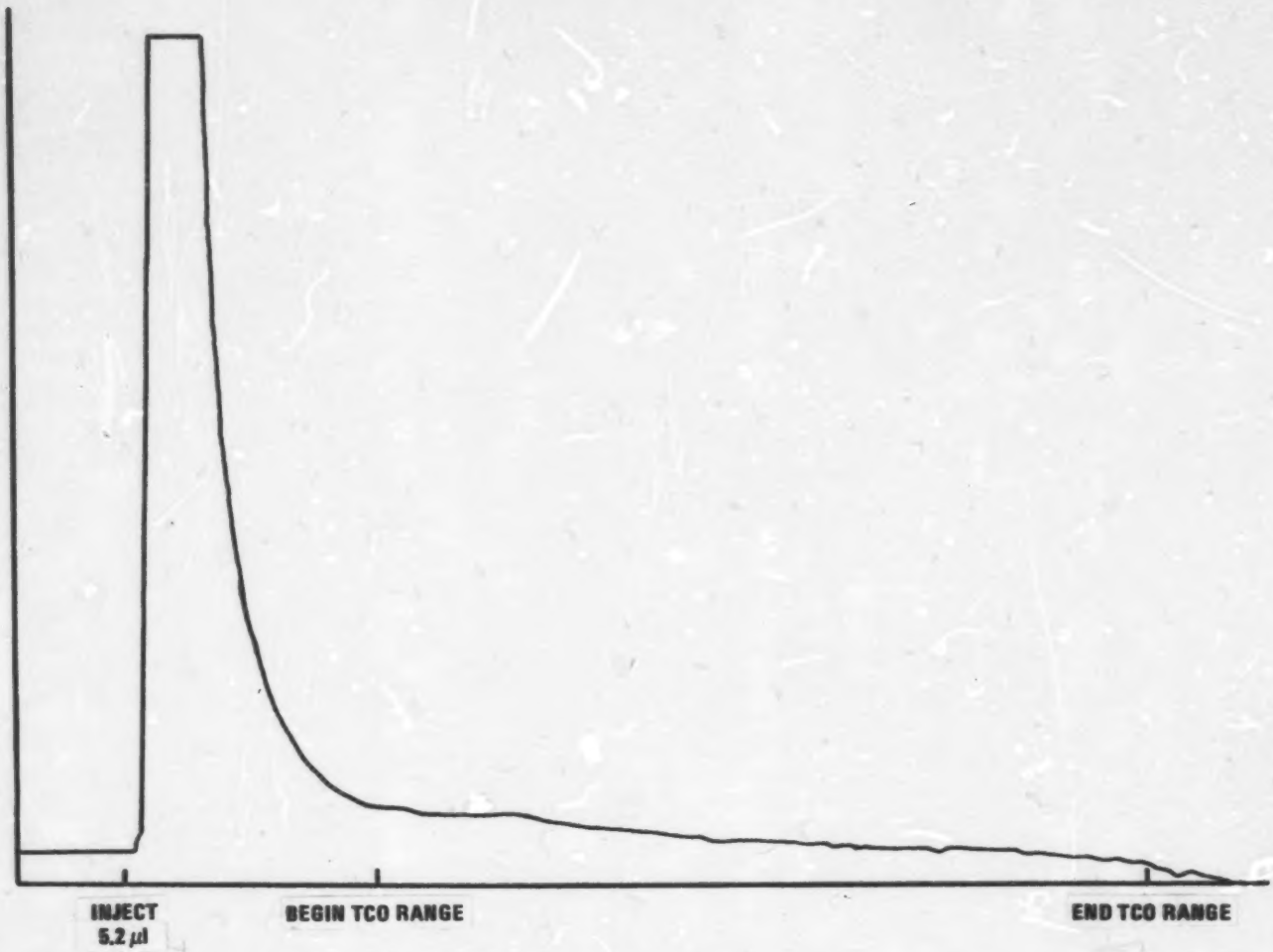

Figure 3. Methylene chloride blank.

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ml samples. It is obvious that cleaning beyond the first methylene chloride extraction is desirable in order to avoid a large blank value. It is also apparent that the quality control test suggested in the Level 1 manual should be run after extraction to ensure resin cleanliness and that this cleanliness cannot be assumed. A sample of the concentrated extract from one of the first methylene chloride cleaning extractions was examined by GC/MS. The major components of the extract were identified as napthalene, one or more substituted decalins, ethyl styrene, and various butyl or diethyl benzenes. Minor components included small fragments of the polymer chain. The bulk of these components were removed from the resin with the first methylene chloride wash.

The other feature to be noted from the GC traces is that for the second extraction chromatogram there are no distinct peaks. If this trace is compared with the methylene chloride blank, it is obvious that material was eluted in the TCO range. This broad background signal can be observed in the first extraction chromatogram as well with the additional distinct peaks superimposed on top of the broad signal. Electronic integrators tend to treat this broad type of signal as baseline while integrating only those peaks meeting the criteria of the integrator algorithm. This effect was studied using a Perkin-Elmer Sigma 10 Integrator. The results for the two integration algorithms available, valley to valley and forced basepoint, are listed in Table 2 as well as the cut and weigh data for the same sample.

TABLE 2. TCO AS A FUNCTION OF INTEGRATION METHOD

Method	TCO (Total mg in 10 ml extract sample)
Valley to Valley[a]	0.9
Forced Base Point[a]	2.0
Cut and Weigh[b]	6.8

[a]Utilizing Perkin-Elmer Sigma 10 Integrator. Valley to Valley is the most common integration method. Forced Base Point attempts background correction.

[b]Cut and Weigh includes full deconvolution of solvent blank.

While the forced basepoint method attempts to correct for the background, it still yields a value far smaller than that obtained by the cut and weigh method. Quantitative determination of this broad background signal along with the well-resolved peaks is an important part of the actual TCO and cannot be ignored. A method by which the actual background (methylene chloride blank) is subtracted from the chromatogram of interest is to be preferred.

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The blank from clean XAD-2 is apparently also dependent on the time between final cleaning and actual use. A sample of resin was received from EPA-RTP which had been cleaned for twice the recommended time for Level 1 procedures and stored under methanol for 14 months. The methanol was decanted and concentrated. A GC/MS study of this concentrate reveals the presence of 1,2-diethyl benzene, ethyl styrene, napthalene, and low molecular weight polystyrene fragments as the TCO materials. Evidently, these components were formed by slow desorption from the resin over the 14 months or by a slow decomposition process.

Determination of TCO was carried out on clean resin samples heated over a temperature range of 85°-183° C. The TCO results are tabulated in Table 3, and the extrapolated TCO values versus temperature for a 400 ml sample as used in a SASS train are shown in Figure 4. It is obvious from the graph

TABLE 3. TCO DATA, HEATED SAMPLES

Temperature	Sample[a]	mg TCO/sample	mg TCO/400 ml resin
85°C	unconcentrated extract	Not Measurable	----
	concentrated[b] extract	1.4	14
120°C	unconcentrated extract	Not Measurable	----
	concentrated extract	1.5	15
140°C	unconcentrated extract	16	161
	concentrated extract	3.9	39
153°C	unconcentrated extract	Not Run	----
	concentrated extract	6.5	65
156°C	unconcentrated extract	Not Run	----
	concentrated extract	8.5	85
183°C	unconcentrated extract	6.5	74
	concentrated extract	8.5	97

[a]All resin samples were 40 ml, with the exception of the 183°C run (35 ml).

[b]Total methylene chloride extract concentrated to a final volume of 10 ml.

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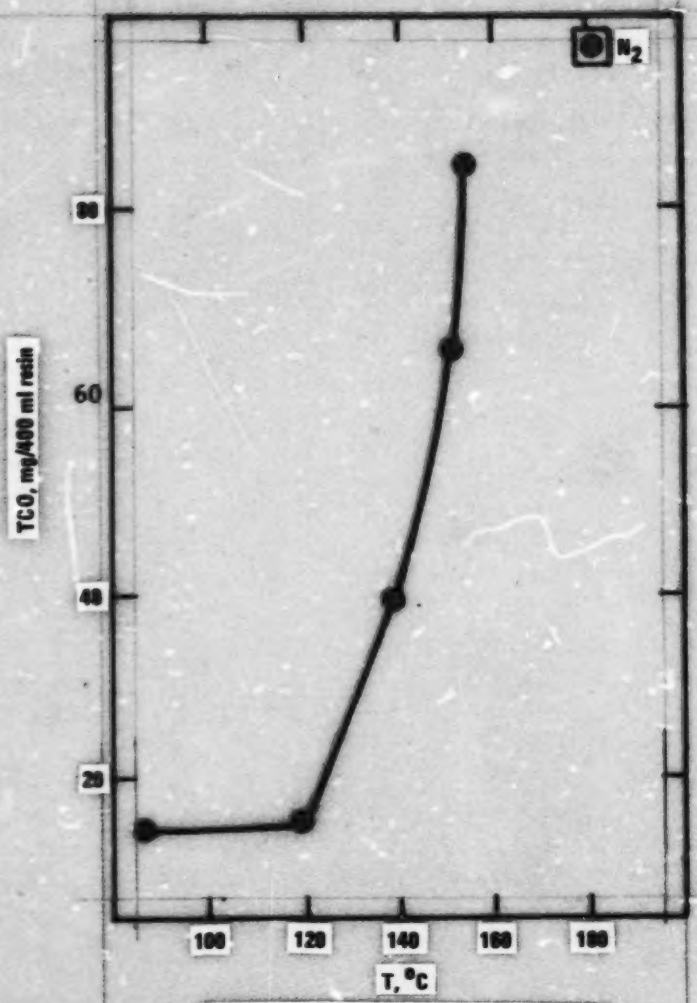

Figure 4. TCO versus temperature.

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that above a threshold temperature, the TCO value rises very rapidly. This emphasizes the importance of keeping the resin cartridge cooled during a sampling operation. Should the resin be heated much above ambient temperature, the measured blank from an unused resin cartridge will not be indicative of the true blank. The same pattern of peaks was observed in the TCO range in almost all cases, indicating that the same process of decomposition/desorption is taking place in each case, with the major variable being the amount of material produced. Resin samples heated above 120° C took on a characteristic light brown color which remained even after extraction with methylene chloride. The intensity of the brown color seemed to increase proportionally with the heating temperature of the resin. The concentrated extracts of these washes had a yellow-brown color as well.

The results of the GRAV determination for three of the heated resin extracts are listed in Table 4. The amount remaining after evaporation of

TABLE 4. GRAV DATA, HEATED SAMPLES

6-1/2"

Sample	mg/10 ml of concentrated extract	mg/400 ml resin (extrapolated)
85°C concentrated extract	1.0	10
156°C concentrated extract	14	140
183°C concentrated extract	11	126

1.0 ml of extract was a little over 1 mg for both the 156° C and 183° C runs. The residue was a brown oil. Not enough residue was left from the 85°C run to weigh, nor was any visible in the flask. The infrared spectra of the GRAV fractions were all similar to that of the 156° C run shown in Figure 9. This is particularly interesting to note in the case of the 183° C run which was done under nitrogen. The presence of a carbonyl band suggests that oxygen was present at some time, perhaps as a contaminant in the nitrogen, as some form of residual oxygen in the resin itself, or by the GRAV fraction being oxidized by atmospheric oxygen during sample workup.

In order to determine whether the oxygen in the air has an effect on the amount of TCO material produced, a resin sample was heated to 183° C under a nitrogen flow of 300 ml/min. As can be noted from Figure 4, the TCO value for this run falls below the curve outlined by the samples heated under airflow. A possible explanation for this phenomenon is that oxygen may take part in the decomposition process by attacking the polymer and initiating an "unzipping" process where the polymer systematically breaks down into smaller pieces. If oxygen is present in low concentrations, the number of sites of attack are low and thus the overall rate of decomposition is lowered. This is not to suggest that oxygen attack is the primary mode of decomposition, but rather that it is one of several possible mechanisms.

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Samples extracted from the heated resins were studied by infrared spectroscopy and GC/MS in order to determine the types of compounds extracted. Some of the GC/MS results from the 156° C extract are included here as an example. Figure 5 shows the GC trace of the sample and the ion density trace for species with mass/charge 77 amu, indicative of species containing a benzene ring. Mass spectral data for this chromatogram are listed in Table 5, and two example mass spectra are shown in Figures 6 and 7. All seven mass spectra from this run exhibit some or all of the pattern 77, 91, 105, 119, 133, etc., characteristic of alkyl benzenes. None of the major components appeared to contain oxygen. Several of the spectra indicate unsaturation in the alkyl chain portion of the species. All of the species in the TCO range appear to contain only one ring, while some material which elutes beyond the upper limit of the TCO range contains two benzene rings. Data on some of the unresolved material which elutes "between" the peaks indicate that these are also alkyl benzenes. Because of incomplete resolution by the GC, peaks may actually consist of several geometrical isomers which elute close to each other, thus making positive structure assignment difficult at best.

Previous studies of the thermal decomposition products of polystyrene carried out by other investigators were done with samples heated to 400° to 1100° C until they completely decomposed. Analysis of the pyrolized products indicated that the majority were merely monomer units or components similar to monomer. The proposed mechanism of decomposition is one in which a piece of the polymer splits off as a free radical causing scissions in the backbone chain. Further abstraction of hydrogen causes more scissions. In this manner, the polymer "unzips" itself into various smaller-size fragments of the polymer chain.

The infrared spectrum of clean XAD-2 resin and that of the gravimetric fraction from the resin heated to 156° C are shown in Figures 8 and 9. Note that in the first spectrum there is not obvious evidence of the presence of oxygen, e.g., carbonyl. The -OH band at 3450 cm^{-1} is due to water in the KBr pellet. The second spectrum has a broad adsorption above 3100 cm^{-1}, a strong peak at 1700 cm^{-1}, and a series of peaks between 1350 and 1100 cm^{-1}, all of which indicate the presence of oxygen, possibly in the form of a carboxylic acid. Because organic acids are not particularly volatile, it is likely that any that were formed during the run would remain in the gravimetric fraction. In addition, organic acids do not "chromatograph" particularly well, and so would quite possibly elute beyond the time window of the TCO determination.

The next step in the thermal stability study was to take some of the clean resin and heat it to obvious decomposition in an air stream for 4 hours. A glass tube attached to the top of the column served to direct the air flow into a cold trap cooled by dry ice/acteone. In this manner, the volatile components of the resin decomposition could be trapped and identified. A GC/MS run on some of the material collected in this manner indicated the presence of various alkyl benzenes as well as a substantial amount of styrene monomer. Incomplete resolution by the GC again made identification of specific compounds impossible, but the ion patterns indicate that the species are various forms of alkyl benzenes.

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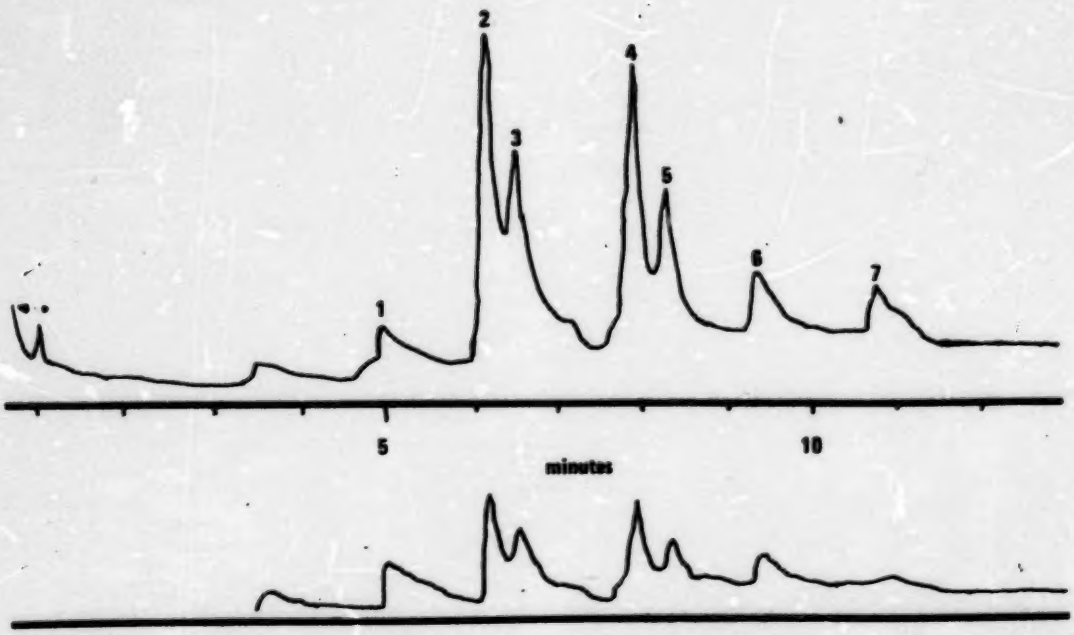

ABOVE: GAS CHROMATOGRAM OF EXTRACT CONCENTRATE TAKEN FROM RESIN SAMPLE HEATED TO 156° C. COLUMN, 2-4% OV-101, TEMP. PROGRAM 90° ISOTHERMAL FOR 2 min., 8°/min. TO 240°.

BELOW: RELATIVE ION ABUNDANCE MONITOR, SET FOR MASS 77.

Figure 5. GC/MS chromatogram and ion abundance trace.

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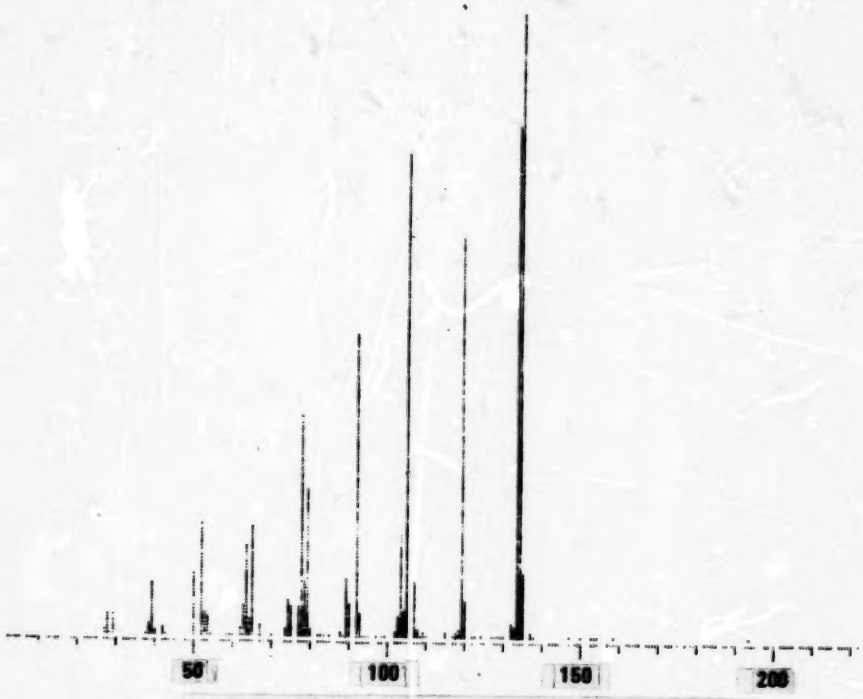

Figure 6. Mass spectrum of peak number 2.

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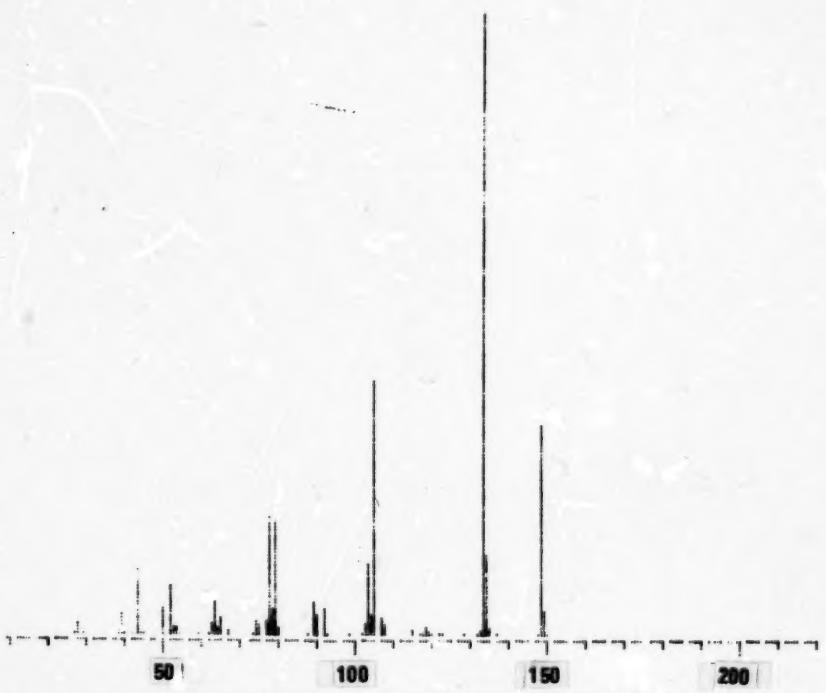

Figure 7. Mass spectrum of peak number 4.

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TABLE 5. GC/MS DATA, MAJOR MS PEAK FOR 153°C EXTRACT

--- PEAK #1 ---		---------- Peak #2 ----------		---------- Peak #3 ----------					
Mass	Abundance	Mass	Abundance	Mass	Abundance	Mass	Abundance	Mass	Abundance
51.2	23.5	51.2	17.8	103.2	17.0	51.2	20.4	107.1	16.9
77.2	66.5	65.2	17.5	105.1	76.6	77.2	38.4	119.2	21.9
105.1	100.0	77.1	35.0	119.2	63.6	79.1	24.5	131.2	21.0
117.2	32.9	79.1	23.4	133.1	80.8	91.2	52.5	132.3	21.0
120.2	44.1	91.2	48.2	134.2	100.0	103.2	28.9	133.1	100.0
						105.1	59.0	134.2	88.3

--- Peak #4 ---		--- Peak #5 ---		--- Peak #6 ---		---------- Peak #7 ----------			
Mass	Abundance	Mass	Abundance	Mass	Abundance	Mass	Abundance	Mass	Abundance
77.1	19.7	77.1	23.5	51.2	21.1	43.2	22.4	119.2	26.4
79.1	18.5	79.1	16.8	77.1	38.8	76.1	16.1	122.2	21.8
105.1	40.4	103.2	15.8	105.1	67.8	77.1	33.9	147.2	100.0
133.1	100.0	105.1	36.2	122.2	16.8	91.2	31.6	162.1	35.1
148.3	33.4	133.1	100.1	133.1	100.0	105.1	45.4		
		148.3	29.1	148.3	31.6				

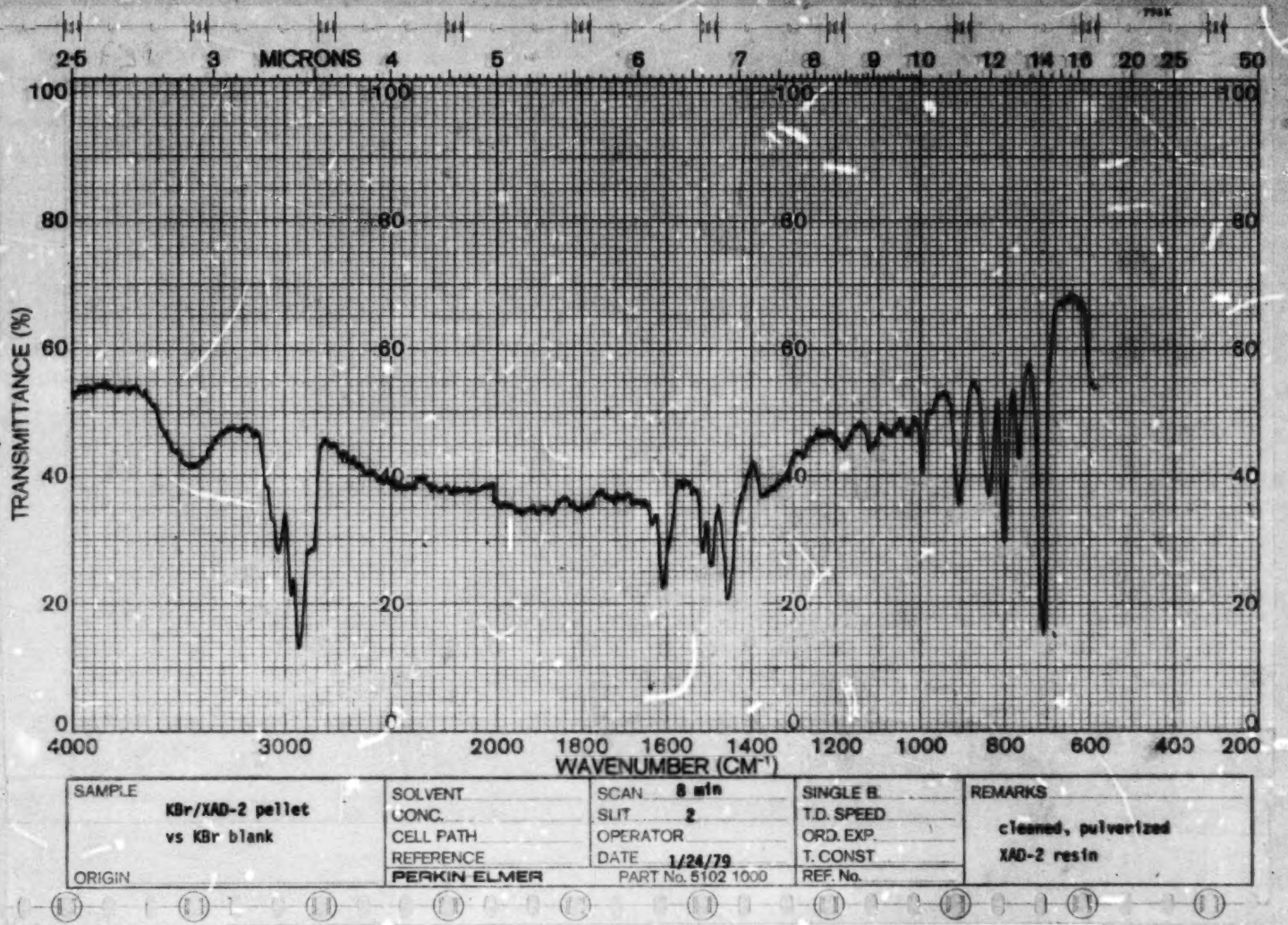

Figure 8. IR spectrum of XAD-2 in KBr vs. KBr.

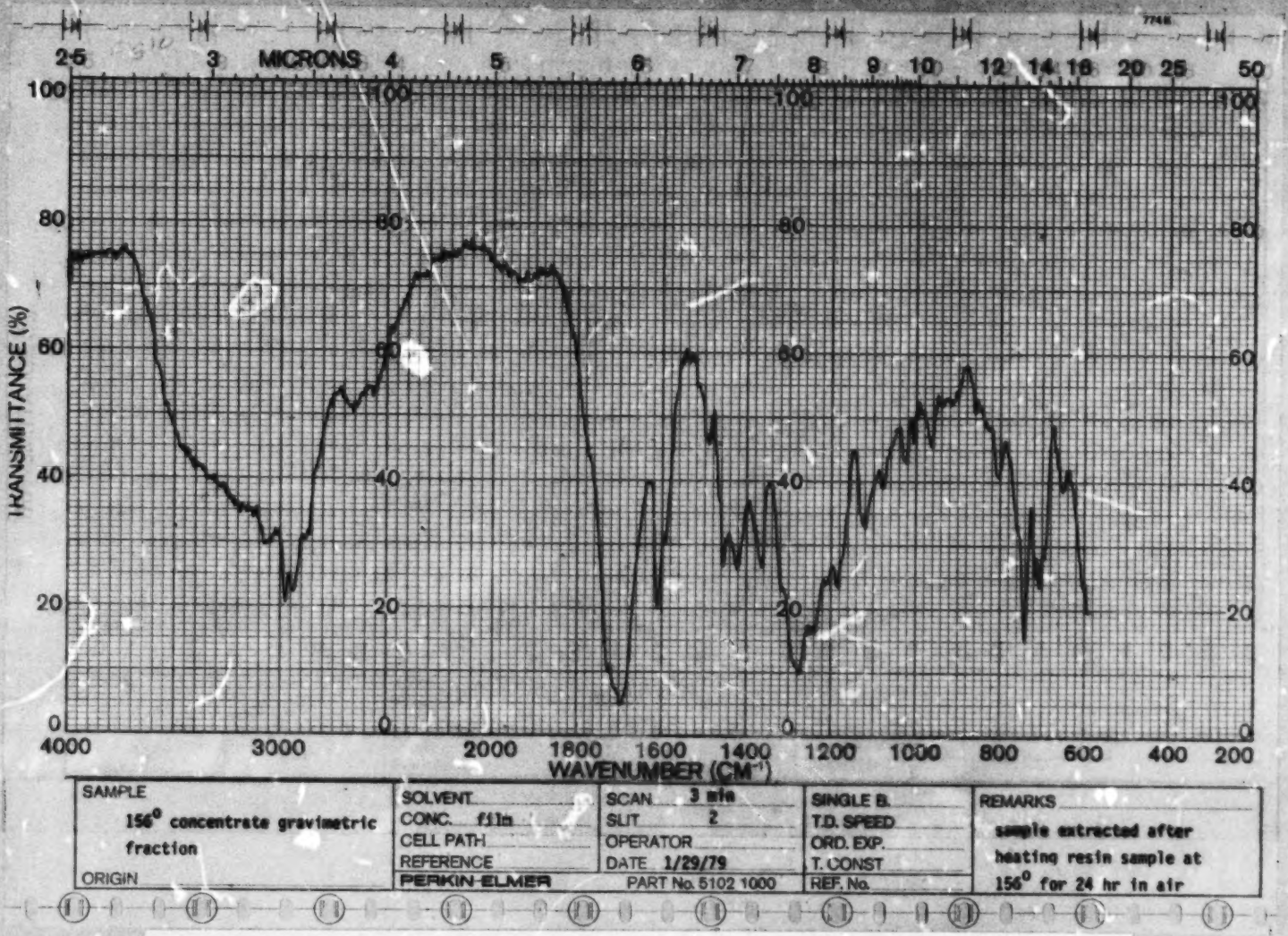

Figure 9. IR spectrum of GRAV fraction from 156° run.

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In a previous study (Personal communication, Larry Johnson, EPA-RTP) of the thermal stability of XAD-2 resin, samples of clean resin were subjected to a flow of dry nitrogen gas at temperatures of 20°, 40°, and 60° C. The volume of gas used was 6.53 ± 0.03 standard cubic meters. No mention of the total heating time was made. The resin samples were then extracted with methylene chloride, and the weight of material extracted was determined by evaporation to dryness of 150 ml of extract in a tared container at ambient conditions. An actual TCO determination as outlined in the Level 1 SASS procedure was not carried out. The residue from the 150 ml of extract was separated by an LC procedure into four fractions containing aliphatic hydrocarbons, aromatics, polar (oxygenated) material, and very polar compounds (carboxylic acids). The aromatic fraction for each temperature run was examined by LRMS and HRMS, and was found to contain alkyl benzenes, small polymers of styrene and fragments of polymers. Both the relative and absolute quantities of these materials increased as the resin temperature increased, indicating that either a thermal decomposition or desorption of material was taking place. The species found in this low temperature study were similar to those found in the present study.

In a report (3) to the EPA concerning the use of a SASS train for sampling emissions from two coal-fired power plants, several infrared spectra were included to demonstrate the type of data in the subsequent workup from the sampling run. The IR spectrum of the extract taken from the XAD-2 cartridge used in one of the runs is reproduced in Figure 10. This spectrum is particularly interesting because it is nearly identical to that produced by the gravimetric fraction of the sample heated to 156° C in our laboratory. These spectra are included to point out an inherent problem which could arise while using the XAD-2 cartridge in a SASS train operation. If improper cooling is applied to the cartridge, enough extractable material may be produced by the resin itself to make an appreciable contribution to the total sample extracted from the resin. The sample taken from the energy source was examined further by GC/MS and was found to contain alkanes, alkenes, phthalates, fatty acid methyl esters, C_2-styrenes, C_3-styrenes, napthalene, benzoic acid, and methyl benzoate. The last five species are reported to have come from the resin itself, as determined by GC/MS on the extract of a previously unused resin sample. It is apparent from the GC/MS data in the present study that several of these species could have also been formed from the resin itself by an inadvertant lack of cooling for the SASS train sorbent module during the run. If the source components to be sampled are present in a low concentration in the subsequent resin extract compared to these "interfering" species, detection and identification could be greatly hindered by this large blank value. It appears evident that special precautions as to the cleaning procedure and thermal history of the resin need to be taken to make the actual analysis as accurate as possible.

One other test of resin stability regarding the TCO blank was carried out. Two clean resin samples of about 30 ml each were placed in two round bottom flasks (100 ml). Several 5 mm diameter glass beads were added to one of the flasks. The vessels were then sealed and agitated on a mechanical shaker for 5.5 hours. The resin samples were extracted with methylene chloride for 24 hours and the extracts concentrated and sampled for TCO

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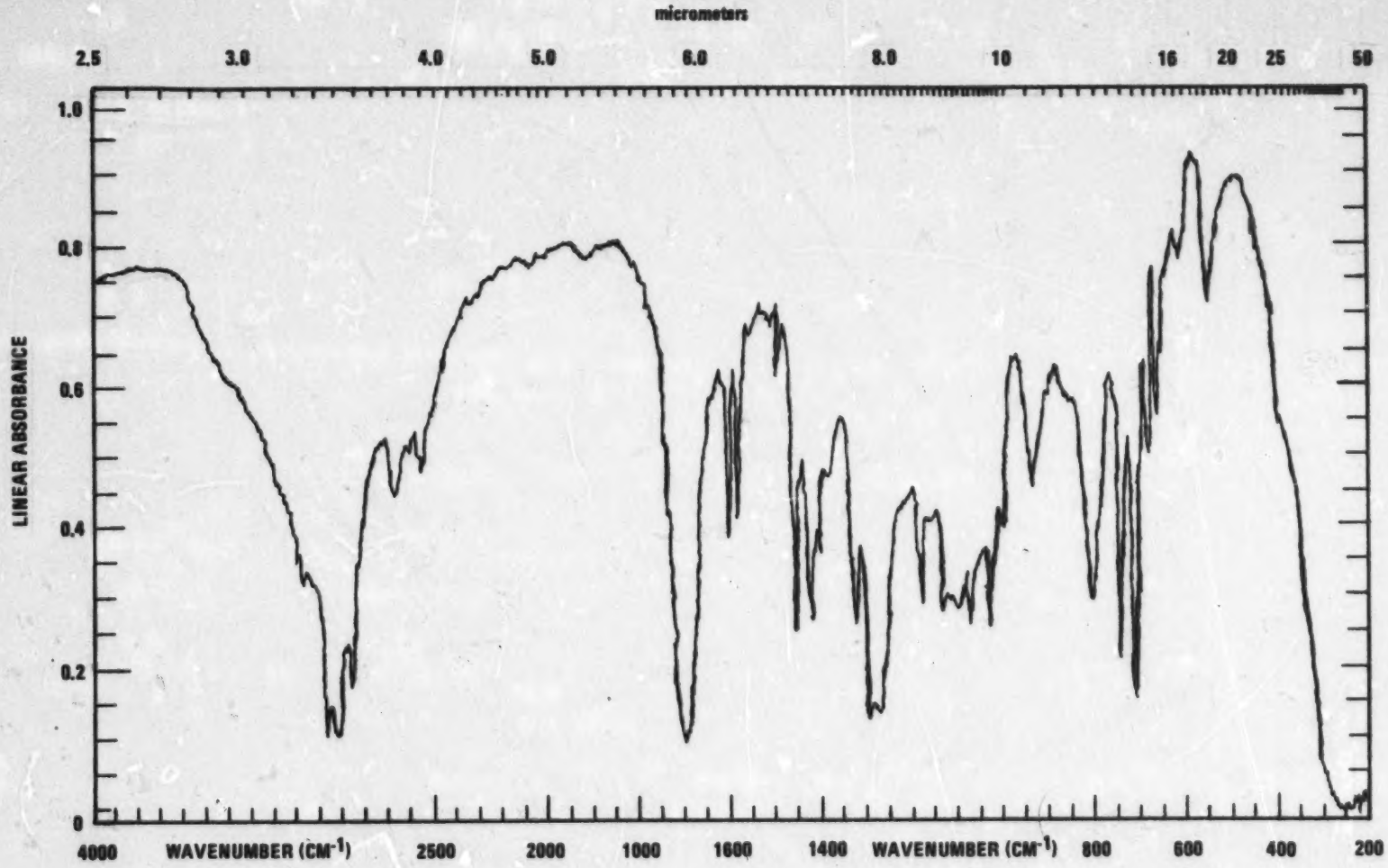

ABISCISSA	ORDINATE	SCAN TIME 12 mins.	REP SCAN —— SINGLE BEAM ——
EXPANSION 1	EXPANSION 1	RESPONSE 1	TIME DRIVE —— PRE SAMPLE CHOP
SUPPRESSION X	%T X ABS ——	SLIT PROGRAM N	OPERATOR DATE 1/10/76
SAMPLE	REMARKS ATTENTUATE USED	SOLVENT ——	CELL PATH ——
ORIGIN		CONCENTRATION THIN FILM	REFERENCE

Figure 10. IR spectrum of unfractionated extract from XAD-2 used in sampling run.

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material. The results were that the sample agitated with no glass beads showed no TCO material while the sample agitated with the glass beads yielded a TCO equivalent to only 2 mg/400 ml resin. This TCO material was a broad, unresolved peak across the TCO time window, thus it appears that within the limits of physical stability, the measured TCO value is not dependent on the physical handling of the resin.

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Section 3

CONCLUSIONS AND RECOMMENDATIONS

There are several points to be made about the stability of XAD-2 resin for use in a SASS train:

1) Extensive cleaning is apparently necessary just prior to use if one is to avoid a large residual blank. This can be monitored by examining the TCO material remaining in the cleaning extraction solvent. Care must be taken to ensure that what appears to be a baseline signal from each of these extracts is, in fact, baseline and not a broad signal due to unresolved material.

2) Long term storage of clean XAD-2 resin does not appear to be viable. Measurable amounts of TCO material either desorb from the resin or are formed in a process involving slow polymer degradation.

3) Storage up to several months may be feasible, but the Level 1 quality control test should always precede use. Physical handling appears not to be a major source of blank material.

4) The thermal stability of XAD-2 with regard to use for trace analysis is especially poor above a certain threshold value. Special precautions should be taken to ensure that the resin is not heated much beyond ambient temperature (25° C) if a significant blank is to be avoided.

5) Should the resin be heated inadvertantly during the sampling procedure, the components which may be expected in the TCO fraction are various alkyl benzenes. The concentration of these will depend on the length of time the resin was heated, the actual temperature of the resin, and possibly the nature of the gas stream being sampled.

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Section 4

EXPERIMENTAL

Samples of XAD-2 resin from Lot 2-9154 (Rohm and Haas, Philadelphia, PA) were cleaned by successive Soxhlet extraction with deionized water for 48 hours, methanol for 48 hours, and fresh methylene chloride every 24 hours until a sample of the concentrated extract showed no measurable material in the TCO range. The clean resin was then air-dried at room temperature and stored until needed. All glassware used in the resin cleaning process was cleaned in alcoholic KOH, rinsed, and heated to 600°C for 2-4 hours in order to rid it of any adsorbed organic material.

Resin samples of approximately 40 ml volume were heated in the apparatus shown in Figure 11. The column consisted of three pieces of Pyrex glass tubing 150 mm long and 25 mm i.d. joined with appropriate clamps. Section B contained glass beads of 5 mm diameter. Section C contained 40 ml of clean resin separated from Section B by glass wool and a wire mesh. Sections B and C were wrapped with heating tapes controlled by separate power supplies. Air was taken from a compressed air tank, passed through a drying tube containing anhydrous calcium sulfate, and admitted through Section A at a rate of 300 ml/min. The heated glass beads served to preheat the air before it came into contact with the resin. The temperature of the resin bed was monitored with two thermometers inserted to varying depths in the resin. Due to the low thermal conductivity of the resin, about 2 hours were required to get the resin up to the desired temperature. During high temperature runs, the rubber gaskets in the clamps were found to be decomposing and contaminating the resin. Another all glass column (300 mm long and 25 mm i.d.) was used for the experiments above 140°C. For the 156° C run, the sample was flushed with dry nitrogen at 300 ml/min while the resin was heated to the desired temperature, and then the gas suppply was switched to air at 300 ml/min for 24 hours. All other samples were run totally under air or nitrogen as indicated. After heating, the resin samples were Soxhlet extracted for 24 hours with methylene chloride. The bulk of this extract was finally concentrated to a volume of 10 ml.

Total Chromatographable Organic (TCO) content was determined essentially by the method outlined in the Level 1 Procedures Manual (1). A Varian Model 1700 gas chromatograph equipped with flame ionization detectors was used. The columns were 180 cm long and 0.32 cm o.d. stainless steel packed with 10% DC-200 on Chromsorb 750 (100/120 mesh). Determinations were done by operating the GC isothermally at 40° C for 6 minutes and then programming at 20° C/min to a final temperature of 250° C. The GC response was calibrated with a solution containing normal C_8, C_{10}, and C_{12} hydrocarbons in concentrations similar to those of the TCO materials in the samples. Injection volumes were no larger than approximately 5 µl. Solutions

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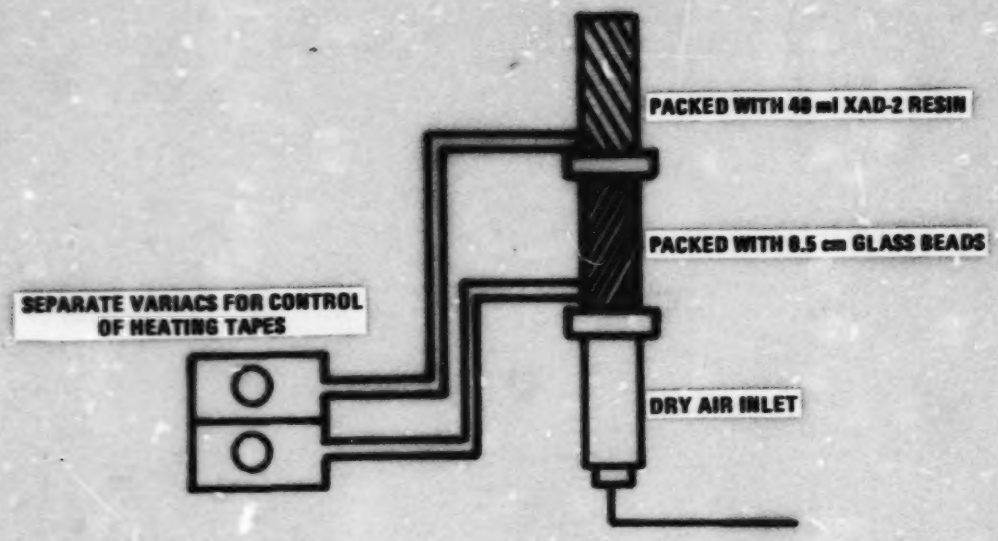

Figure 11.Apparatus for heating XAD-2 resin.

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of normal C_7, C_{16}, and C_{18} hydrocarbons were used to determine the elution temperature limits of the TCO window. The upper elution temperature limit defined by the n-C_{17} peak was determined by interpolation between the C_{16} and C_{18} peaks. A blank methylene chloride injection was run along with each TCO determination to account for background signal due to column bleed. This background signal was subtracted from the extraction chromatogram before quantitative TCO determination by the cut and weigh method.

The gravimetric (GRAV) fraction was determined by measuring 1.0 ml of the concentrated extract into a previously weighed 5 ml round bottom flask. The solvent was then removed on a rotary evaporator and the flask reweighed. Duplicate samples were run since only a small amount of material remained after evaporation.

The GC/MS data were obtained with a Hewlett-Packard Model 5992A GC/MS system and the infrared spectra were taken on a Perkin-Elmer Model 297 infrared spectrometer.

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References

1. D. E. Lentzen, D. E. Wagoner, and E. D. Estes. IERL-RTP Procedures Manual: Level 1 Environmental Assessment Second Edition Draft. EPA- 68-02-2156, Research Triangle Institute, Research Triangle Park, North Carolina, 1978. 143 pp.

2. F. A. Lehaman and G. M. Brauer. Analysis of Pyrolyzates of Polystyrene and Poly(methlmethacrylate) by Gas Chromatography. Anal. Chem., 33:673, 1961.

3. Radian Corporation. Collection and Analysis of Organics Emitted From Coal-Fired Power Plants. EPA 68-01-3702, Radian Corporation, 8500 Shoal Creek Boulevard, Austin, Texas, 1978. 30 pp.

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